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FIRST QUARTERLY REPORT

THE REACTIONS PERTAINING TO ZINC-SILVER AND CADMIUM-SILVER BATTERIES

JPL 951887

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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ABSTRACT

Preliminary results show that the insoluble product formed on the electro-oxidation of Zn in neutral KNO_3 is about 50% $Zn(OH)_2$. Heavily amalgamated Zn produces an anode which discharges at a reasonable rate. The An(Hg) electrode shows promise as a high-rate anode.

High quality AgO has been produced electrochemically and approximate activation energies for thermal decomposition of AgO and Ag_2O have been determined.

The objectives of the contract are three-fold:

(1) The characterization of cadmium and zinc anodic reaction products.

(2) The thermal decomposition of silver oxide.

(3) The deposition of silver on zinc anodes.

This report deals with parts of the first two objectives and will be divided into: (A) The investigation of the insoluble products of the electrochemical oxidation of zinc and (B) the thermogravimetric investigation of AgO and Ag_2O.

A. ELECTROCHEMICAL OXIDATION OF ZINC

Introduction

The precipitate formed by addition of base to a Zn(II) solution contains an amount of hydrogen corresponding to the quantity of water or hydroxide in the precipitate. This hydrogen can be determined if the solution contains ^3H_2O by measuring the radioactivity of the solid. The relative amounts of $Zn(OH)_2$ and ZnO present can be estimated by assuming that $Zn(OH)_2$ is the only hydrogen-containing species in the material.

We have estimated that precipitates formed with KOH contain 15-20% $Zn(OH)_2$ while those formed with NH_3 contain 85-100% $Zn(OH)_2$ (1). Since the method by which the precipitate is formed affects the nature of the product, the present work is directed toward determining the composition of the material formed by the electrochemical oxidation of zinc in neutral and KOH solutions.

Experimental

Sheet electrodes were cut from Electronic Space Products Grade 6N zinc, 0.25 mm thick. Porous electrodes were prepared by electrodepositing zinc on Ag mesh from a KOH solution saturated with ZnO. Amalgamated electrodes were made in two forms: (a) Sheet zinc was immersed either in a solution of

$Hg(NO_3)_2$ or in Hg until a layer of mercury adhered to the surface, (b) Zinc was dissolved in Hg either by letting the metal stand in a Hg pool until the zinc dissolved or by reducing ZnO electrochemically at the Hg surface.

A small cell was constructed of Lucite to hold one Zn and one AgO electrode and 3-4 ml of electrolyte solution. The electrodes were 4 cm^2 in area and were mounted 2 mm apart. Zn electrodes used in this configuration were usually wrapped in a single layer of polypropylene separator material.

Cells were also constructed by suspending the electrodes in a 50 ml beaker and covering them with electrolyte solution. This configuration was used exclusively with the amalgam electrodes.

Electrolyte solutions were 10 F KOH, 10 F KOH saturated with ZnO, or 2 F KNO_3.

Tracer experiments were run with KNO_3 solutions to which appropriate amounts of ^3H_2O had been added. These experiments were performed in the Lucite cell. The product was collected within the polypropylene envelope and was treated as previously described (1).

Electrodes were discharged spontaneously in cells using a AgO cathode or by supplying external power from a battery while employing a Pt cathode. Current was controlled manually.

Results and Discussion

Attainment of complete oxidation of Zn proved to be very difficult in most cases. Porous electrodes were found to be only partially discharged when reaction apparently stopped. When the surface layer of oxide was removed, a hard, gray layer of zinc was found which seemed quite unreactive. Application of external power to speed reaction caused hydrogen evolution. Some commercial electrodesbehaved similarly although the zinc was supposed to be somewhat amalgamated.

Sheet zinc anodes formed a black surface layer after a fairly short period of discharge in KOH solutions; at this point the cell current decreased sharply. The behavior was observed with AgO and with Pt cathodes; therefore, silver deposition was not a factor. Microscopic examination of the layer did not suggest a simple etching of the electrodes as is found when zinc reacts with fairly concentrated HCl. Furthermore, the metal beneath the surface layer reacted preferentially with HCl while the black material dissolved only very slowly. The composition is as yet unknown, however the black color indicates that it is not simple ZnO.

Sheet zinc anodes produced a white solid product when discharged in neutral KNO_3 solution. This material behaved as the ZnO we expected.

Tracer experiments were made with KNO_3 solutions because these gave the type of product we expected. Porous electrodes were used for convenience, although the solid electrodes might be of some advantage. Only a few results are available with this system and precision is poor. The preliminary evidence indicates that the product is about 50% $Zn(OH)_2$, although individual results ranged from 30-60%. In any case, the hydroxide content seems to be greater than that found by direct chemical precipitation with KOH.

Amalgamated sheet zinc anodes behaved satisfactorily in KOH-ZnO electrolyte solutions, but formed an interesting product. A brittle layer of deep blue material formed between the Hg surface and the zinc metal. The material retained its blue color as long as it was in contact with moist KOH but became gray when dry. Addition of water caused the blue color to reappear. When the KOH was washed away, the blue faded rapidly and could not be recovered. This material, when dry, was the

color of sand and was translucent. Although the blue product seems dependent on the presence of Hg during the reaction, no Hg was detected in the material. Here, too, the nature of the cathode has no obvious effect.

Zinc dissolved in Hg formed an interesting electrode which might have some practical use. The solubility of Zn in Hg has not yet been determined; however, amounts corresponding to one ampere-hour (38 milliequivalents) have been dissolved in 4 ml of Hg. Electrodes of this kind have produced current-densities of 850 ma/cm^2 with a AgO cathode; the latter is probably limiting in this case. The Zn(Hg) electrode can be recharged and, in fact, is most readily formed by reducing ZnO electrochemically in a KOH solution. Complete discharge of the electrode occurs consistently.

The recharge capability and the very high current densities obtainable suggest that the Zn(Hg) electrode may have practical applications. There is the further possibility that more active metals, e.g., alkaline earth metals, might be dissolved in Hg to provide an electrode of considerably higher potential than is generally possible in an aqueous electrolyte system.

Conclusions

Preliminary experiments suggest that the insoluble product formed on the electro-oxidation of Zn in neutral KNO_3 is about 50% $Zn(OH)_2$. Adequate recovery of product from alkaline solutions has not yet been accomplished.

Heavily amalgamated Zn provides the best anode in terms of rate of discharge. The product formed has not been identified, but is apparently different from that formed in the absence of Hg.

The Zn(Hg) electrode shows promise as a high discharge-rate electrode. The possibility of electrodes employing alkaline earth metals instead of Zn is worth considering.

Proposed Work

The investigation of the product formed by electro-oxidation of Zn will be continued. Attempts will be made to recover product from alkaline solution in sufficient quantity to give reproducible analyses. Thermogravimetric and IR investigations will be used to support tracer results.

B. THERMAL DECOMPOSITION OF AgO and Ag_2O

Experimental

Thermograms have been repeated on some of the AgO previously prepared. AgO was prepared electrochemically (2) on Pt-grid electrodes and increasing-temperature thermograms run. Similar thermograms were obtained for AgO supplied by W. Ames Chemical Works. Methods employed have been described previously (1).

Results and Discussion

It was previously reported (1) that AgO prepared on a Pt grid was quite different from that prepared on a Pt foil. A new sample was prepared on a Pt grid and analysis refutes the former conclusion, the product being of excellent purity--in the neighborhood of 99.5% AgO. Thermograms of the material were run at three different heating rates (2.7°/min., 4.7°/min., and 8.7/min.) and approximate energies of activation calculated by the method described by Flynn and Wall (3). These values are:

$$2\,AgO = Ag_2O + \tfrac{1}{2}\,O_2 \qquad E = 60 \text{ kcal/mole}$$

$$Ag_2O = 2\,Ag + \tfrac{1}{2}\,O_2 \qquad E = 47 \text{ kcal/mole}$$

A thermogram of a portion of a AgO electrode formed in KOH was run and was found to contain almost no AgO and only about 25% of the expected amount of Ag_2O. The electrode had been formed from silver powder at a current density of 100 ma/cm^2 until gas was evolved. The current density was obviously too high so new electrodes are being formed at about 4 ma/cm^2.

Proposed Work

Constant-current thermograms at temperatures other than 140° will be run. Samples will be chemically, electrochemically, and commercially prepared materials. Pressed pellets of the materials will be used to see if pressing affects thermal behavior. Increasing-temperature thermograms will be made at different heating rates to compare apparent activation energies.

REFERENCES

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